



Standard Guide for Measurement of Gases Present or Generated During Fires¹

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This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 Analytical methods for the measurement of carbon monoxide, carbon dioxide, oxygen, nitrogen oxides, sulfur oxides, carbonyl sulfide, hydrogen halides, hydrogen cyanide, aldehydes, and hydrocarbons are described, along with sampling considerations. Many of these gases may be present in any fire environment. Several analytical techniques are described for each gaseous species, together with advantages and disadvantages of each. The test environment, sampling constraints, analytical range, and accuracy often dictate use of one analytical method over another.

1.2 These techniques have been used to measure gases under fire test conditions (laboratory, small scale, or full scale). With proper sampling considerations, any of these methods could be used for measurement in most fire environments.

1.3 This document is intended to be a guide for investigators and for subcommittee use in developing standard test methods. A single analytical technique has not been recommended for any chemical species unless that technique is the only one available.

1.4 The techniques described herein determine the concentration of a specific gas in the total sample taken. These techniques do not determine the total amount of fire gases that would be generated by a specimen during conduct of a fire test.

1.5 *This standard is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.*

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

[D123 Terminology Relating to Textiles](#)

[D1356 Terminology Relating to Sampling and Analysis of Atmospheres](#)

[D2036 Test Methods for Cyanides in Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3612 Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography](#)

[D6348 Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared \(FTIR\) Spectroscopy](#)

[D6696 Guide for Understanding Cyanide Species](#)

[D6888 Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis \(FIA\) Utilizing Gas Diffusion Separation and Amperometric Detection](#)

[D7295 Practice for Sampling and Determination of Hydrogen Cyanide \(HCN\) in Combustion Effluents and Other Stationary Sources](#)

[D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide](#)

[E84 Test Method for Surface Burning Characteristics of Building Materials](#)

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E176 Terminology of Fire Standards

E535 Practice for Preparation of Fire-Test-Response Standards

E603 Guide for Room Fire Experiments

E662 Test Method for Specific Optical Density of Smoke Generated by Solid Materials

3. Terminology

3.1 *Definitions*—Definitions used in this guide are in accordance with Terminology D123, Terminology D1356, Terminology E176, and Practice E535 unless otherwise indicated.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *batch sampling*—sampling over some time period in such a way as to produce a single test sample for analysis.

3.2.2 *combustion products, n*—airborne effluent from a material undergoing combustion; this may also include pyrolysates.

3.2.2.1 *Discussion*—

combustion products without mass, such as heat or other radiation, are not addressed in this guide.

3.2.3 *fire test, n*—a procedure, not necessarily a standard test method, in which the response of materials to heat or flame, or both, under controlled conditions is measured or otherwise described.

3.2.4 *sample integrity*—the unimpaired chemical composition of a test sample upon the extraction of said test sample for analysis.

3.2.5 *sampling*—a process whereby a test sample is extracted from a fire test environment.

3.2.6 *test sample*—a representative part of the experimental environment (gases, liquids, or solids), for purposes of analysis.

4. Significance and Use

4.1 Because of the loss of life in fires from inhalation of fire gases, much attention has been focused on the analyses of these species. Analysis has involved several new or modified methods, since common analytical techniques have often proven to be inappropriate for the combinations of various gases and low concentrations existing in fire gas mixtures.

4.2 In the measurement of fire gases, it is imperative to use procedures that are both reliable and appropriate to the unique atmosphere of a given fire environment. To maximize the reliability of test results, it is essential to establish the following:

4.2.1 That gaseous samples are representative of the compositions existing at the point of sampling,

4.2.2 That transfer and pretreatment of samples occur without loss, or with known efficiency, and

4.2.3 That data provided by the analytical instruments are accurate for the compositions and concentrations at the point of sampling.

4.3 This document includes a comprehensive survey that will permit an individual, technically skilled and practiced in the study of analytical chemistry, to select a suitable technique from among the alternatives. It will not provide enough information for the setup and use of a procedure (this information is available in the references).

4.4 Data generated by the use of techniques cited in this document should not be used to rank materials for regulatory purposes.

5. Sampling

5.1 More errors in analysis result from poor and incorrect sampling than from any other part of the measurement process (1, 2).³ It is therefore essential to devote special attention to sampling, sample transfer, and pretreatment aspects of the analysis procedures.

5.2 *Planning for Analysis*—Definitive answers should be sought and provided to the following questions during the planning stage: (1) *Why* is the sampling (analysis) being performed? (2) *What* needs to be measured? (3) *Where* will samples be taken? (4) *When* does one sample? (5) *How* are samples collected? (3).

5.2.1 All aspects of sampling and analysis relate to the fundamental reasons for performing the analysis. Analysis of combustion products is normally performed for one of the following reasons: for research on the composition of the gases; to relate directly to flammability, smoke generation, toxic or irritant effects; to study mechanisms of combustion; or for development of test equipment. The experimenter should decide exactly what type of information the analysis must provide. The necessary detection limits, acceptable errors, and possible or tolerable interferences must be determined.

5.2.2 A representative sample must be obtained; however, sampling must not interfere with the test (for example, sampling could alter the atmosphere in an animal toxicity experiment or in a smoke measurement device). The size and shape of the test chamber affects the possible location and number of sampling probes.

³ The boldface numbers in parentheses refer to the list of references appended to this standard.

5.2.3 Single or cumulative samples may be adequate for many requirements; however, a continuous monitor may be desirable for the determination of concentration-time dependence, or in the case of analysis of reactive species (for example, hydrochloric acid (HCl)).

5.2.4 Collection and transport of samples must be accomplished in such a way that the analyses properly reflect the nature and concentration of species in the combustion gas stream. Heated sampling lines made from an inert material are often required. Direct sampling and immediate analysis are preferable to retention of the sample for later analysis. Filtration of combustion gases prior to analysis may be necessary for some applications, but may be totally incorrect for other cases (see 5.9).

5.3 *Test Systems*—Many devices of various sizes can generate “fire gases” for analysis (4, (5)). These systems include large-scale facilities (fire situations simulated on a 1:1 scale (see Guide E603 and Ref (6)); large laboratory-scale tests (for example, Test Method E84); laboratory-scale chambers (for example, Test Method E662 (7, 8)); and microcombustion furnace or tube furnace assemblies (2, (9)).

5.3.1 In general, the combustion devices (test chambers) fall into three categories:

- (1) closed chambers (for example, Test Method E662);
- (2) open chambers (for example, a full-scale room burn);
- (3) flow-through systems (for example, Test Method E84).

5.3.2 Different test chamber sizes and configurations require different methods of sampling and analysis. Appropriate analytical procedures and equipment must be selected. In a full-scale fire experiment the sampling frequency and detection level and accuracy may not need to be the same as in a small laboratory-scale experiment.

5.4 *Reactivity of Fire Gases:*

5.4.1 Fire gases to be analyzed range from relatively inert and volatile substances, such as carbon monoxide (CO) and carbon dioxide (CO₂), to reactive acid gases such as hydrogen fluoride (HF), HCl, and hydrogen bromide (HBr). Other species frequently determined are oxygen, the sulfur-oxide species sulfur dioxide (SO₂) and sulfur trioxide (SO₃); the nitrogen-containing species hydrogen cyanide (HCN), nitric oxide (NO), and nitrogen dioxide (NO₂); and hydrocarbons and partially oxidized hydrocarbons.

5.4.2 The following potential problems must be avoided or minimized by proper design of the sampling system and choice of materials of construction:

- (1) Reaction of the gaseous products with materials used in sampling lines and test equipment that could lead to loss of sample and potential equipment failure;
- (2) Adsorption, absorption, or condensation of gaseous products in the sampling system or on particles trapped in the filtration system;
- (3) Reaction among species present in the gaseous sample;
- (4) Interferences caused by species in the sample, other than the product being analyzed, that respond to the analytical method.

5.5 *Sampling Frequency*—The frequency of sampling is based primarily on the information sought. Most requirements will be met by one of the following three sampling modes:

- (1) The quantity formed during the experiment is determined by collecting one time-integrated sample (2);
- (2) The concentration is determined at a limited number of time points during the experiment (10);
- (3) The concentration is determined either continuously or with sufficient frequency to represent it as a function of time (6, 8, 10, 11).

5.5.1 The two techniques used most commonly in the past have been the single, integrated sample and sampling at fixed time intervals. However, techniques for continuous analysis of certain species are now readily available (CO, CO₂, and oxygen (O₂)); while continuous analysis of other compounds of interest have been reported (12).

5.5.2 The integrated sampling technique entails collection of all the products (or a continuous sample from the gas stream) into an unreactive sampling bag such as polytetrafluoroethylene (PTFE) or absorption of the species of interest in an appropriate solvent in an impinger for the duration of the experiment. Analyses are then performed on the contents of the bag or trapping medium (9). Water-soluble species such as HCl or HBr have been collected in solution impingers over the duration of the experiment, enabling analysis of the “integrated” sample. The gas flow rate through the impinger and the liquid volume determine the buildup of acid gas in the solution (the solubility of the species at the given gas flow rate should be verified). The integrated sampling techniques provide either the “average” concentration of the particular species over the duration of the test or, for certain flow-through test procedures, a measure of the total amount of that species produced in the experiment. In this latter case, a total gas flow measurement is required.

5.5.3 Continuous or frequent, periodic sampling is often desirable. This limits further reaction of reactive species (such as HCl, HBr, and HCN), and is useful for studies of time-dependent, cumulative effects of toxic gases (such as CO) on animals.

5.5.4 Samples of combustion gas can be collected sequentially for subsequent instrumental analysis. An electrically activated multiport stream selection valve or a manifold of solenoid valves can be used to sequentially divert the combustion gas into a series of gas collection devices. This collection procedure can be automated by using a valve sequence timer or a multipole relay timer (13, 14).

5.5.5 For noncontinuous sampling of combustion gases, the frequency of sampling is often determined by the instrumentation. For example, using gas chromatography, sampling will be dependent on the residence time of species in the instrument. Sampling of species at time intervals using gas syringes, plastic sampling bags, sorption tubes, or the like, with analyses to be performed later, is not dependent on analysis time.

5.5.6 The volume of frequent or continuous gas samples removed must not significantly affect the concentration of remaining species. In small test chambers and some flowthrough systems, the volume of gas available for sampling is limited.

5.6 *Sampling Sites:*

5.6.1 The number and the locations of sampling sites are determined by the extent of analytical information sought and by the configuration of the test chamber (15, 16). To obtain representative samples from an NBS smoke density chamber, intake ports in one study (11) were located at three heights inside the chamber. The sample streams were then combined before being introduced into the analyzers. Previous experiments had demonstrated that significant stratification occurred in the chamber during part of the test. In a full-scale bedroom fire test (6), four gas sampling probes were used.

5.6.2 Guidelines developed for the monitoring of the emission of pollutants (1, 17, 18) can be utilized for the demonstration of the mass flow rates of combustion products through ducts. Traverses across the ducts (in a steady-state experiment) with a CO- or CO₂-probe can be useful for determining whether a need exists for multiple sampling sites.

5.7 *Sampling Probes:*

5.7.1 Sampling probes must withstand exposure to the test environment and must not affect the integrity of the sample with respect to the substances being analyzed. Care should be exercised in heating probes of PTFE; temperatures above 250°C may affect their physical properties.

5.7.2 Probes fabricated from PTFE, PTFE-lined stainless-steel, glass-lined stainless-steel, unlined stainless-steel, borosilicate glass, or quartz tubing are frequently used for sample extraction from combustion or pyrolysis systems. Stainless steel should not be used with combustion products containing hydrogen halides since it reacts with these compounds. Glass and quartz react with fluorides; the latter substance can be extracted with PTFE probes if the atmospheric temperature is low enough. If the temperature is high, an alternative sampling technique would be placing absorption tubes at the sampling point, housing the tubes in an ice-water bath, and trapping HF upstream of all sampling lines and pumps (13, 14).

5.7.3 Probe and transfer lines should be heated to prevent losses of some combustion products such as total hydrocarbons due to condensation and HBr, HCl, nitrogen oxide (NO_x), and SO₂ due to solubility in condensed moisture (see Sections 7 and 9).

5.7.4 Commercially available gas syringes, evacuable glass or metal containers, plastic sample bags, and sorption tubes are often used for intermittent grab sampling (19, 20, 21).

5.7.4.1 The sorption tube should be appropriate for the gasses to be analyzed. Glass-lined stainless-steel sorption tubes filled with glass beads coated with a strong base solution give excellent collection efficiency for the hydrogen halides (13, 14). Glass-lined stainless-steel tubes packed with p-2,6-diphenylphenylene oxide⁴ (a porous polymer that withstands high temperatures) are effective in the collection of hydrogen cyanide, organic nitriles, and other organics generated in fires.

5.8 *Sample Volume, Sampling Rate:*

5.8.1 In any sampling technique, the same volume is determined by the sensitivity of the method used for analysis, the detection level sought, the concentration of the species to be analyzed, and the precision required for the determination.

5.8.2 In continuous sampling, the sampling rate is partially determined by the desired response time. To minimize the response time, small-diameter transfer lines are used and all in-line devices (for example, filters and scrubbers) are kept to minimum volumes. A pressure drop may result from use of small diameter sampling lines.

5.8.3 Response time cannot be calculated exactly from sample line volume and gas flow rate because of the viscous nature of gas flow in the transfer lines and the continuous mixing of gas in sensor compartments. Response times can be determined experimentally by making a rapid change in gas concentrations at the sampling probe inlet and determining the time to a given response (usually 90 % or greater). Furthermore, all instruments have an intrinsic response time independent of sampling procedure.

5.8.4 Information pertaining to sampling rate and sampling volume is contained in Refs (21) and (22).

5.9 *Sample Pretreatment:*

5.9.1 Pretreatment of the sample must not affect sample integrity with respect to the species being analyzed. Pretreatment is used for the following purposes:

(1) The removal of species that would interfere with the performance of the detectors or would react with the species being analyzed, and

(2) Chemical conversion of the species present in the sample to those that are detected by the sensors.

5.9.2 Removal of particulate matter may be required for certain analyses. Particulates interfere with optical measurements; they can deposit in transfer lines and valves, possibly causing malfunctioning; and they can adsorb gases of interest or chemically react with sample gases.

⁴ Tenax, a trademark of Enka BV, Ressort Patentwesen, Postfach 100149, D-5600, Wuppertal, Federal Republic of Germany, available through gas chromatography supply houses, has been found suitable for this purpose.

5.9.2.1 Loosely compacted PTFE-fiber filters have been found to be useful for the removal of particulate matter. Fiber filter thimbles of PTFE have been used in sampling probes (11). In that system, filter medium was also contained in a chamber where several sample streams were combined prior to analysis.

5.9.2.2 Glass-fiber filters can be used with many types of gaseous samples; however, they cannot be used for samples containing HF. Cellulosic filters should be used with caution because of their reactivity toward a variety of substances.

5.9.2.3 Filters must be heated to the same temperature as the sampling probe and sample transfer lines to minimize adsorption and condensation in the filtration media.

5.9.2.4 In some circumstances, filtering material should *not* be present before the analysis point. An example is the measurement of acid gases using a liquid impinger as the trapping and analysis medium. A filter before the impinger would remove acid gases by adsorption onto liquids and particulates on the filter. Care must be taken that the impinger does not clog with particulates, and that oils or particles in the impinger liquid do not interfere with analysis.

5.9.3 Some analyzers require the removal of water vapor from the sampling line for proper operation or for valid data analysis purposes. Water vapor can be removed by a cold trap, by absorbent media, or by selective permeability media.

5.9.3.1 A cold trap will remove any gases, such as the acid gases, that are soluble in water. The vapor pressure at the temperature of the cold trap of any gas to be measured must also be considered. Due to these factors, this technique is generally limited to use in O₂, CO, and CO₂ analysis systems.

5.9.3.2 The low capacity of most absorbent media generally limits the application of this technique to second stage desiccation, following a cold trap. Water vapor as well as other gases, especially water soluble ones can also be removed. Conversion of NO₂ to NO has been observed (22). Due to these considerations, the absorbent media technique is generally limited to use in O₂, CO, and CO₂ analysis systems.

5.9.3.3 The performance of selective permeability driers in removing or not removing classes of compounds present in the sample stream has been studied (23, 24). Water and, in general, water soluble hydrocarbons are removed. Many inorganic gases, CO, CO₂, and others, are not removed.

5.9.4 Some analyses require chemical conversion of species to that detected by the analytical sensors (for example, reduction of chlorine to chloride). Most chemical conversions are performed within the detector (for example, reduction of NO₂ to NO (see Section 9)).

5.10 *Sample Transfer:*

5.10.1 Sample transfer is usually effected by pumping devices. Sample integrity must be retained during transfer. Materials suitable for sample probes and pretreatment devices are usable for transfer lines. For certain applications, stainless steel (no exposure to acid gases) and glass (no exposure to HF) can be used.

5.10.2 The internal surfaces of the pumps must be inert to the substances being transferred. Interior parts coated with PTFE are commonly used. In the transfer of acid gases, the impingers or scrubbers used for the adsorption of these species should precede the pumps in the sample transfer system.

5.10.3 To retain sample integrity, transfer lines leading to analyzers for nitrogen oxides, hydrogen halides, sulfur dioxide, and hydrocarbons should be heated to prevent condensation and reduce adsorption.

5.10.4 Quantitative sample transfer requires flow rate determination. Rotameters and orifice-type meters are generally useful in combustion gas analysis.

5.11 *System Maintenance:*

5.11.1 Preventive maintenance is essential for analysis systems in which the gas streams contain reactive and condensable components.

5.11.2 In addition to normal instrument maintenance, the following preventive steps are recommended:

5.11.2.1 Filters should be examined and replaced before they become heavily loaded with particulate matter. Some filters should be replaced after each experiment.

5.11.2.2 The inside surfaces of gas transfer lines, valves, and pumping devices should be examined and cleaned periodically. Deposits should be removed with appropriate solvents.

5.11.2.3 Rotameters should be examined to ascertain that the floats are moving freely. The rotameter tubes and the floats should be periodically cleaned with appropriate solvents.

6. Analytical Methods for Carbon Monoxide, Carbon Dioxide, Oxygen, and Nitrogen

6.1 The gases carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), and nitrogen (N₂) will be considered as a group, since several of the analytical methods to be discussed can be applied to more than one of them, sometimes simultaneously. The techniques to be described are gas chromatography, infrared spectrophotometry, and “other methods” including electrochemistry.

6.2 *Gas Chromatography:*

6.2.1 *General Description*—Gas chromatography is an ideal batch method for analyzing nonreactive gases in combustion products (25). These gases can be separated on columns with solid stationary phases operated isothermally and detected using thermal conductivity (TC) detectors. Some of the column configurations and alternative detectors are described below.

6.2.2 *Apparatus and Procedures:*

6.2.2.1 Apparatus requirements are modest. A basic gas chromatograph with standard temperature controls and thermal conductivity detector can be used. A gas sampling valve is a very useful accessory. Temperature programming, automated valve operation, electronic integration, etc., are convenient but not necessary.

6.2.2.2 Complete separation of all of these gases normally requires the use of two columns—a molecular sieve, which separates O₂, N₂, and CO but irreversibly absorbs CO₂ at normal operating temperatures; and a porous polymer column which readily separates CO and CO₂ from air but does not resolve O₂ and N₂. The two columns have been used together, in various configurations and with column-switching valves, to achieve complete separation of the gases (26).

6.2.2.3 An arrangement, using dual columns and a column-switching valve, has been successfully used to analyze O₂, N₂, CO, and CO₂ gases (27). Total analysis time was approximately 15 min.

6.2.2.4 Concentric single columns, consisting of an inner and an outer column of different packing, are also available (28). These will separate O₂, N₂, CO, and CO₂ in a single pass. The use of such columns eliminates the column-switching valve required in the dual-column arrangement; however, their use to date has been limited.

6.2.2.5 The sensitivity of the gas chromatographic method depends on sample size, the type of detector, and temperature and filament current for TC detectors. Thermal conductivity detector filaments will deteriorate if large air samples are repeatedly measured at high current. These gases can be measured at concentrations as low as 0.05 %.

6.2.2.6 Lower concentrations of CO can be detected by converting CO to methane (CH₄) by catalytic hydrogenation (29). The CH₄ is then detected, using a flame ionization detector (FID).

6.2.3 *Advantages and Disadvantages:*

6.2.3.1 The major limitation of gas chromatography for monitoring combustion products is its inherent restriction to batch sampling, since each analysis requires several minutes to complete. Therefore, only a limited number of points can be obtained during a test. However, samples can be collected, intermittently during a run, in suitable gas-tight containers (for example, syringes with close-off valves or gas sampling bags) and the contents analyzed at a later time. The relative nonreactivity of these gases allows them to be stored for extended periods of time before analysis.

6.2.3.2 The gradual build-up of organic pyrolysis and combustion products in the analytical columns may result in eventual degradation of performance. When this occurs, columns can be purged overnight at elevated temperatures or back-flushed; however, after a long period of use, it may be necessary to replace the column.

6.3 *Infrared Analysis:*

6.3.1 *General Description:*

6.3.1.1 Infrared (IR) methods are useful for continuously monitoring the concentration of CO or CO₂ in fire gases. Symmetric diatomic molecules, such as oxygen and nitrogen, cannot be detected because they are infrared inactive.

6.3.1.2 Infrared analysis is based on absorption of radiation at specific wavelengths when the species of interest is present. By varying the length of the sample cell, gas concentrations from a few parts per million up to 100 % can be analyzed.

6.3.2 *Apparatus and Procedures:*

6.3.2.1 A standard (dispersive) infrared spectrophotometer can be used to measure CO or CO₂ by operating with the monochromator fixed at a particular wavelength; or a conventional infrared spectrum of the gas mixture can be obtained.

6.3.2.2 A nondispersive infrared (NDIR) analyzer continuously monitors a single wavelength or wavelength band (30, 31). Such instruments are often less expensive than dispersive instruments; however, they are restricted to a particular wavelength or chemical species. (See Test Method D3612.)

6.3.3 *Advantages and Disadvantages:*

6.3.3.1 Interferences can occur in infrared analyses when absorption bands of other components in the sample overlap the absorption band of the compound being analyzed. The magnitude of the interference is highly dependent on the specific instrument and on the relative concentrations of the gases.

6.3.3.2 The major interferences found are of CO for CO₂ and vice versa. For most applications, CO interference with CO₂ analysis is minor. The interference of CO₂ with a CO measurement can be reduced (if necessary) by incorporating a trap (for example, soda-lime or granular lithium hydroxide (LiOH)) to remove CO₂ from the sample stream before reaching the analyzer.

6.3.3.3 Water vapor can interfere with CO₂ analysis; however, this is not usually a problem. If necessary, a moisture trap in-line can reduce this interference (see 5.9.3). Smoke particulates must be filtered out (see 5.9.2).

6.3.3.4 The instrument readings will be affected by the total gas pressure in the measuring cell. This arrangement is usually adequate if the measuring cell is vented to ambient conditions.

6.4 *Other Methods:*

6.4.1 *General Description*—Electrochemical techniques are available for measuring CO and O₂ (32), but not for CO₂. Such devices are usually designed for air pollution or stack gas monitoring. A standard technique for CO involves oxidation in an electrolytic cell. Techniques for measuring oxygen include galvanic cells, polarographic analyzers, and paramagnetic analyzers.

6.4.2 *Advantages and Disadvantages*—All of these methods can be accurate and specific, but have slower response than the IR methods previously described. Accurate measurement of oxygen concentration with a paramagnetic analyzer requires compensation for the effects of measuring cell pressure.

7. Analytical Methods for Hydrogen Halides

7.1 General Comments:

7.1.1 The analysis of the hydrogen halide gases (hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr)) in combustion atmospheres has always been considered difficult, due primarily to the highly reactive nature of these species. The gases must be analyzed immediately or converted to a stable form to be analyzed at a later time (for example, dissolved aqueous solution in an impinger). The reactivity of these gases has led most workers to limit the length of sampling lines and to ensure that these lines are both heated and prepared from an inert material such as PTFE or glass (33, 34), as described in 5.7. Instead of in-line pumps, gas samples are generally pulled into the analytical device using a vacuum source (33, 35).

7.1.2 The techniques used for the quantitative detection of hydrogen halides (HX) can be classified into three broad categories: (1) “proton-detection devices,” in which the HX is dissociated in solution and the activity of the hydrated proton is analyzed (for example, pH, conductometric); (2) “anion detector devices,” in which the HX is dissociated in solution and the anion is analyzed (for example, ion-selective electrode, titrimetry, and ion chromatography); and (3) “hydrogen halide detection devices,” in which the intact molecule is analyzed (for example, infrared and gas chromatography). These will be discussed in the following sections.

7.2 Proton Detection Devices:

7.2.1 *General Description*—One of the simplest ways to measure the concentration of acid gases in a combustion environment is to draw a portion of the gases into an aqueous solvent and measure the pH of the resulting solution, using a conventional pH electrode. This technique is not specific to any particular species (see below). Another approach involves the measurement in the change of conductance of a solution in which sample gases have been dissolved.

7.2.2 Apparatus and Procedures:

7.2.2.1 Two approaches have been described (12, 35) which use a microelectrolytic conductivity detector originally developed for use in gas chromatography (36). In the approach described by Herrington (12), filtered gases were continually pumped into the conductance cell and continuously monitored. Hileman (35) sampled gases through an 8-port gas-sampling valve, followed by discrete analysis using the conductance cell. The analysis time for a given sample was approximately 30 s.

7.2.2.2 For pH measurement, a research-quality pH meter should be employed.

7.2.3 Advantages and Disadvantages:

7.2.3.1 Simple pH measurement is prone to interferences from any other gases that can generate or remove protons on dissolving in water (that is, CO₂, SO₂, SO₃, HCN, NO₂). Thus, the pH electrode is best used to obtain a value of total acid gas concentration.

7.2.3.2 Many of the interference problems encountered in using pH electrodes are eliminated by using a nonaqueous electrolyte in the conductometric procedures. The conductometric apparatus can be used as a continuous monitor of the hydrogen halide gas; however, frequent calibration is recommended.

7.3 Anion Detection Devices:

7.3.1 *General Description*—The use of ion-selective electrodes (for fluoride, chloride, or bromide) has become increasingly popular for the analysis of hydrogen halides. These types of analyses can be conducted in either a continuous mode (33, 35, 37) or a batch mode (38, 39). Ion chromatography and titration procedures are also available for halide ion analysis.

7.3.2 Apparatus and Procedures:

7.3.2.1 Combustion gases may be continuously bubbled into a solution containing an ion-selective electrode and the anion concentration measured while it is constantly increasing (33). The rate of production of hydrogen halide is determined by differentiating the concentration-versus-time curve. A batch analysis may involve obtaining a gas sample in a syringe containing the dissolving solution (38, 39) or a single time-integrated sample in an impinger solution.

7.3.2.2 Recent advances in ion chromatographic methods have permitted separation of anions (40, 41) with subsequent conductivity measurement of the eluted species. The carbonate anion and various organic acids are interferences for chloride with the conductivity detector if they are not well separated chromatographically. The silver/silver chloride (Ag/AgCl) detector is specific for chloride and bromide with a very low sensitivity for carbonate and other anions. The fluoride detector is a specific detector for fluoride in combustion gas samples (42, 43). The ultraviolet (UV) detector for ion chromatography is sensitive to all anions. With indirect photometric chromatography light-absorbing eluent anions enable the sample anions to appear as negative peaks in the absorbance record (44).

7.3.2.3 A variety of methods involving titration of the hydrogen halides in municipal drinking water (43, 45) have been developed but have not been extensively applied to the analysis of combustion gases (46).

7.3.2.4 Collection tubes containing dry soda lime have proven to be useful for sampling HCl from combustion atmospheres (10). The test atmosphere is sampled over a time period, such as 3 or 5 min, but the interval can be shortened if the concentration of HCl is high. Consecutive samples can be obtained in order to provide a concentration/time plot. The chloride is extracted from the soda lime by water and is analyzed by titration.

7.3.2.5 A continuous analyzer for HCl has been described (47). It employs readily available commercial “stat” titration equipment. The method monitors HCl concentration by continuously titrating chloride ion in an impinger with silver nitrate (AgNO₃).

7.3.3 Advantages and Disadvantages:

7.3.3.1 Ion selective electrodes avoid many of the problems encountered in other HX analyses, since they are ion specific. Anion interferences such as cyanide and sulfide can be minimized with proper consideration of the interfering species. Cyanide and sulfide degrade the electrode membrane, slowing the response and reducing the accuracy. Slight corrosion effects on the electrode can be removed by repolishing. Bromide interferes with the chloride ion electrode; however, chloride does not interfere with the bromide ion electrode, except at very high concentrations of chloride.

7.3.3.2 Ion chromatography may be particularly useful when strong interference from anions causes other techniques to fail. However, this technique has the disadvantage of being noncontinuous.

7.3.3.3 Collection tubes containing dry soda lime can often be used to sample from locations which would be difficult to sample from using solution absorbers or other techniques. They are compact and easy to handle and have high absorption efficiency. Care must be taken to avoid breakthrough due to too high gas-flow rate or high HCl concentration or the tendency to plug up in extremely smokey atmospheres.

7.3.3.4 There are insufficient data yet to accurately describe the advantages and disadvantages of the “stat” titration method; however, it has the potential to be a versatile continuous method for HCl with few problems from smoke particulates or liquids and requiring no calibration gases. Its disadvantages include interferences from other halide and cyanide gases and efficiency of absorption of the HCl.

7.4 Hydrogen Halide Detection Devices:

7.4.1 Hydrogen halides can be analyzed with gas chromatography, however, this is not commonly used because of difficulties with corrosion and poor analysis caused by problems with poorly formed peaks (48).

7.4.2 The gas filter-correlation analysis technique has been developed for a number of gases (49-52). Commercial instruments for HCl are available. The technique also lends itself to in situ measurements, specifically, a beam passed across an exhaust stack section (53, 54). A commercial instrument suitable for full-scale stack measurements is available. Gas-filter correlation analyzers can be designed to minimize the problem of instrument drift. Care must be taken to avoid precipitating the HCl as an aerosol; limited measurements indicate that this is unlikely if the relative humidity in the measuring system is kept below 70 to 80 % (55).

8. Analytical Methods for Hydrogen Cyanide

8.1 Several analytical approaches have been used to measure hydrogen cyanide (HCN). These may be generally categorized as electrochemical, spectroscopic (infrared), colorimetric, gas chromatographic, and flow injection analysis utilizing gas diffusion separation. Additional information for analytical methods is given in Guide D6696.

8.1.1 When fire smoke samples are collected with impingers (sometimes referred to as bubblers) containing 0.1 M sodium hydroxide using Practice D7295, the samples can be analyzed with flow injection analysis described in Test Method D6888 or with a suitable analytical method such as ion chromatography described in Test Methods D2036.

8.2 Electrochemical Methods:

8.2.1 *General Description*—Electrochemical techniques that have been used to measure HCN in fire gases include an amperometric method, two potentiometric techniques (including ion-selective electrodes), and differential pulse polarography. All of these techniques entail measurement of cyanide ion in solution.

8.2.2 Apparatus and Procedures:

8.2.2.1 In the amperometric method for HCN (12), the current flow between two electrodes is measured while HCN is being absorbed into the electrolyte solution. A flow injection method utilizing gas diffusion separation and amperometric detection (see 8.5) can also be used when smoke gas is collected with impingers.

8.2.2.2 The cyanide ion selective electrode has been used widely for HCN measurement (12, 56-59). A silver/sulfide electrode, which measures cyanide ion indirectly, can be used. A “specific-ion meter” or expanded-scale pH meter is necessary for these electrodes.

8.2.2.3 Ion-selective electrodes have generally been used for intermittent analysis, where sample gas is bubbled into the impinger for a specified time (for example, 5 min). However, continuous analysis setups have been explored.

8.2.2.4 Standard titrimetric techniques (60, 61) can also be used for determination of hydrogen cyanide. In the absence of halide ions, cyanide can be titrated potentiometrically using (AgNO₃).

8.2.2.5 Differential pulse polarography (62) can be used for time-integrated or grab sampling of cyanide.

8.2.3 Advantages and Disadvantages:

8.2.3.1 The amperometric technique permits continuous determination of gaseous HCN in the range from 0.1 ppm to greater than 100 ppm. Only H₂S exhibits a major interference using this technique; however, this can be eliminated by using a solid lead carbonate scrubber.

8.2.3.2 The ion selective electrode methods are very sensitive; however, response is slow at low solution concentrations. Sulfide, iodide, bromide, and chloride interfere with the measurement of cyanide, when using the cyanide ion electrode (63). Certain interferences can often be eliminated by a change of the type of electrode used or by the addition of a masking agent to the solution.

8.2.3.3 Titrimetric procedures remain among the simplest techniques for a time-integrated analysis of cyanide in the absence of interfering ions. Interferences in differential pulse polarography include oxygen and compounds containing carbonyl groups.

8.1 *Infrared and Colorimetric Methods:* Several analytical approaches can be used to measure hydrogen cyanide (HCN). Early information can be found in Refs (56-60).

8.1.1 *Apparatus and Procedure:* Direct measurements of HCN can be made with Fourier transform infrared (FTIR) spectroscopy (61). For more information on the determination of gaseous compounds by FTIR spectroscopy, see Test Method D6348. Standard gas cells can be used; however, longer path length, nondispersive infrared instruments are better suited for low concentrations. Gas filter correlation techniques have also been proven useful for HCN analysis (see 7.4.2).

8.3.1.1 Dispersive and Fourier transform (64) infrared spectroscopy have been used to measure HCN gas directly. Standard gas cells have been used; however, longer path length, nondispersive infrared instruments are better suited for low concentrations. Gas filter correlation techniques have also been proven useful for HCN analysis (see 7.4.2). A commercial analyzer is available.

8.3.1.2 Colorimetry has been successfully used in measuring low concentrations of HCN. The standard colorimetric procedures for cyanide are the picrate procedure (65), the pyridine-pyrazolone method (57), and pyridine-barbituric acid (D2036). A simple spectrophotometer is suitable for the colorimetric methods. Instruments have been modified to accommodate flow-through cells for continuous analysis (65).

8.1.2 *Advantages and Disadvantages:*

8.1.2.1 This technique offers a means for continuous analysis of HCN in the gas phase, if interferences can be accounted for or eliminated. Potential interferences to infrared determination of HCN are acetylene, propane, and water vapor.

8.1.3 HCN in fire smoke can also be collected with impingers (sometimes referred to as bubblers) as described in Practice D7295. A known volume of gaseous sample is bubbled through an impinger containing 0.1-M sodium hydroxide solution utilizing a calibrated pumping system. Particulates that may pass through the impinger are captured on a glass fiber filter then recombined back into the impinger solution prior to analysis. During the sampling process, hydrogen cyanide (HCN) is converted to cyanide ion (CN⁻) in the sodium hydroxide solution, and then cyanide is analyzed in the impinger solution using gas diffusion separation and flow injection analysis (FIA) with amperometric detection as described in Test Method D6888 or ion chromatography (IC) as described in Test Methods D2036. Colorimetric (pyridine-barbituric acid) and cyanide-ion selective electrode methods, also described in Test Methods D2036 can be used for screening purposes. The concentration of HCN is calculated as described in Practice D7295. Potential interferences for each of these test methods are described in Practice D7365. Additional information for analytical methods is given in Guide D6696.

8.1.4 *Advantages and Disadvantages:*

8.3.2.1 Potential interferences to infrared determination of HCN are acetylene, propane, and water vapor. This technique offers a means for continuous analysis of HCN in the gas phase, if interferences can be accounted for or eliminated.

8.1.4.1 Colorimetry is limited. Impingers and the required sampling pumps are readily available at most industrial hygiene and air quality laboratories. Practice D7295 to low concentrations and therefore may require dilution was found to be suitable for measuring HCN during combustion of several natural and synthetic matrices including wood, wool, flax, and polyurethane materials (62). Precision and bias data were determined according to a US EPA Field Validation Method 301; the data are summarized in Practice D7295. The determinative step, Test Method D6888 of sample solutions. Colorimetric methods, was evaluated for precision and bias with an interlaboratory study consisting of 10 laboratories as described in Practice D2777 are generally time-consuming. Aldehydes; the interlaboratory data are summarized in Test Method D6888. Alternative determinative steps are available (for example, colorimetry and ion-selective electrode), but they may be more susceptible to interferences (for example, aldehydes, ketones, sulfide, thiocyanate, and sulfur dioxide) are (63). potential interferences. Sample pretreatment and distillation described in Test Methods D2036 may be used to overcome some of these interferences. The methods described in Test Methods D2036 were not validated specifically for fire smoke effluent samples; therefore, it is the responsibility of the user to demonstrate precision and recovery for each sample matrix that is burned.

8.1.4.2 Results from a single impinger produce a single, average concentration for the duration of the experiment, while multiple impingers, required to develop a concentration-time profile, entail additional time and equipment.

8.4 *Gas Chromatographic Methods:*

8.4.1 *General Description*—Gas chromatography can be used effectively to measure HCN in combustion products. Several different columns and types of detectors have been used to give the desired specificity and sensitivity.

8.4.2 *Apparatus and Procedures:*

8.4.2.1 A gas chromatographic method using a thermal conductivity detector (66) was developed for measuring high concentrations of HCN. However, this method had a lower limit of detectability of 0.3 volume %, which would require concentrating HCN for most fire test studies. A concentrator with a thermistor detector has been used (67, 68) to lower the detectable limit of HCN to 10 to 15 ppm per 2-mL injection volume.

8.4.2.2 A flame ionization detector (FID) is more sensitive and specific than either the thermal conductivity (TC) or thermistor type and has been used to measure HCN in a simulated hydrocarbon combustion atmosphere from 10 ppm to several hundred parts per million (69). Hydrogen cyanide in the pyrolysis products of nitrogen-containing fibers has also been measured (70).

8.4.2.3 A nitrogen-specific modification to an alkali-flame (or thermionic) detector gives greatly enhanced sensitivity for nitrogen-containing compounds. It has been used to monitor HCN in an animal exposure chamber containing CO and air (71). It was also used successfully for measurement of HCN during thermal degradation of nitrogen-containing polymeric materials (72).

This detector has also been used to measure HCN trapped from combustion products using glass-lined stainless-steel tubes packed with p-2,6-diphenylphenylene oxide, a porous polymer that withstands high temperatures. For the analysis, the HCN is thermally released from the porous polymer (42).

8.4.2.4 In other studies on the analysis of HCN in the decomposition products of rigid polyurethane (35), the alkali flame detector was tuned with a sample containing normal hydrocarbons (methane through *n*-pentane up to 20 000 ppm) in order to achieve minimal interference from these species.

8.4.2.5 Another gas-chromatographic approach to HCN analysis has been to chemically react the HCN (73, 74) and then measure the resultant product with an electron-capture detector (75).

8.4.3 Advantages and Disadvantages:

8.4.3.1 An advantage of gas chromatography, for most combustion gas studies, is that it requires a small gas sample size. However, analyses are intermittent, rather than continuous, and sample elution times are often several minutes.

8.4.3.2 The flame ionization detector suffers from interference from low molecular weight organic species; and its response is affected by small changes in detector geometry, gas flow rates, etc. The thermionic detector minimizes the hydrocarbon and water interference problems. With a thermal-conductivity detector, water, CO, and CO₂ can interfere with analysis of HCN (depending on the column used).

8.4.3.3 Hydrogen cyanide must be trapped in an impinger, for analysis by the electron-capture detector. Total treatment and analysis time is about 30 min.

8.5 Flow Injection Analysis (FIA) Method:

8.5.1 *General Description*—HCN in fire smoke is collected with impingers containing sodium hydroxide according to the procedures of Practice D7295, then analyzed according to the procedures of Test Method D6888.

8.5.1.1 Test Method D6888 was developed for the analysis of available cyanide in wastewater samples, but can be adapted for the measurement of cyanide in fire smoke effluents when samples are collected in impingers containing 0.1 M NaOH (76). Since HCN is converted to NaCN in the impinger solution, ligand-exchange reagents utilized for wastewater samples are not necessary.

8.5.2 Apparatus and Procedure:

8.5.2.1 Samples are injected into the FIA system for acidification with 1 M H₂SO₄ containing a sulfide removal reagent. Hydrogen cyanide diffuses through a hydrophobic gas diffusion membrane from the acidic donor stream into an alkaline acceptor stream. The captured cyanide is sent to an amperometric flowcell detector with a silver-working electrode. The anodic current measured is proportional to the concentration of cyanide in the standard or sample injected.

8.5.3 Advantages and Disadvantages:

8.5.3.1 This analytical portion of this method was shown to be free of interference and more reliable than colorimetric or selective ion electrode determinative steps (77). There is minimal or no interference from other fire gases and the detection limit is less than 2 µg/L CN in the impinger solution. The procedure takes considerably less time than colorimetric methods.

8.5.3.2 Results from a single impinger produce a single, average concentration for the duration of the experiment, while multiple impingers, required to develop a concentration-time profile, entail additional time and equipment.

9. Analytical Methods for Nitrogen Oxides, Sulfur Oxides, and Carbonyl Sulfide

9.1 Oxides of nitrogen include nitric oxide (NO) and nitrogen dioxide (NO₂). Fire gases contain mostly NO; NO₂ formation is usually a secondary oxidation process. Sulfur oxides include sulfur dioxide (SO₂) and sulfur trioxide (SO₃), the former being the more prevalent in fire gases generated from sulfur-containing materials.

9.2 Nitrogen Oxides:

9.2.1 Chemiluminescence:

9.2.1.1 *General Description*—Chemiluminescence is the principle of operation of several process analyzers for nitrogen oxides. Either NO or total nitrogen oxide content (NO_x) can be measured. The amount of NO₂ is calculated from the difference between NO and NO_x.

9.2.1.2 Sampling is continuous in either the NO or NO_x mode; however, sampling volumes are large. Samples of NO cannot be stored for later analysis. Both NO and NO₂ measurements can be obtained simultaneously in an electrochemical-type analyzer equipped with two cells.

9.2.1.3 *Interferences*—Significant interference from other nitrogen-containing compounds such as HCN, can occur if high temperature (760°C) thermal converters are utilized for the NO_x determination (7864). This has been eliminated, in most of the instruments, by using a catalyst at lower temperatures. The sensitivity to non-NO_x nitrogen-containing species potentially present in the samples of interest should be established before the unit is used for making measurements. It appears that water and CO₂ may act as third-body quenchers (7965) and H₂ can be a source of interference in the stainless-steel converter (8066). Interference from halogen containing compounds can also occur (8167).

9.2.1.4 *Advantages and Disadvantages*—Many instruments for analysis of nitrogen oxides were designed for ambient-air monitoring. Therefore their analysis range can be too low for direct fire gas determinations. Instruments for high concentration NO_x are available.

9.2.2 Ion Chromatography: